Present and future fluxes of nitrogen, phosphorus and carbon from catchments to lakes in a boreal landscape

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CONTENTS

ABSTRACT

This work is focused on how external factors influence fluxes of the key nutrients, nitrogen, phosphorus and carbon in boreal streams and rivers and thus control the annual and inter-annual dynamics in chemistry and biology of the recipient lakes. Approaches and research tools applied in the study include long-term monitoring, field measurements, budget calculations, comparative studies, statistical modeling and mechanistic process-based modeling.

Study on the influence of climatic factors showed that precipitation and air temperature can explain a high proportion of the annual and seasonal variability in river nutrient concentrations. However, the relationships between the weather and water quality are often masked by time lags in hydrology, seasonality and complexity of all the affecting factors. To define the study to the influence of hydrology on nitrate (NO_3) in rivers, NO_3 concentrations and loads were compared between summer seasons with high and low discharge. The highest concentrations were observed during the high discharge summers when the summer NO_3 load comprised more than half of the annual load. This caused remarkable changes on the nutrient levels in the recipient lake during high discharge summers, affecting the ecosystem of the lake during the growing season.

The mass balance calculations for the recipient lake, Lake Pääjärvi, showed that the mean annual retention for total phosphorus (tot P) in the lake was as high as 74% while the values were lower for total nitrogen (tot N) (27%) and total organic carbon (TOC) (34%). It is evident that Pääjärvi has the effect of decreasing nutrient concentrations downstream. The results of the study of carbon (C) in a chain of five lakes highlighted the effect of the lake size and its setting on the catchment. Hydrological import and export of TOC dominated the carbon fluxes especially in the small drainage lakes in the middle of the chain. In-lake processes presumably had greater influence on the C fluxes in the large lakes in the study. On the landscape scale, small lakes (area < 1 km^2) were important in the net accumulation of C in the sediments, since they were responsible for 56% of the net C accumulation in all the lakes although they formed only 14% of the entire lake area. On the other hand, the large lowland lakes (size class 10 – 50 km^2) played a more important role in the fluxes of CO_2 to the atmosphere.

In the future, the increasing frequency of heavy precipitation events and wet/dry periods may further strengthen the variability in timing and magnitude of nutrient loads, but there will be variation in the response of lakes and rivers. This will largely depend on the characteristics of the lakes and rivers as well as on the properties of their catchments.

LIST OF ORIGINAL PAPERS

This thesis is based on the following papers, which in the text are referred to by their Roman numerals:

I) Arvola, L., Hakala, I., Järvinen, M., Huitu, E. & Mäkelä, S. 2002: Effects of weather conditions on water quality in two small boreal rivers. Large Rivers 13, Arch. Hydrobiol (Suppl.) (Large Rivers) 141:195-208.

II) Einola, E., Rantakari, M., Kankaala, P. Kortelainen, P., Ojala, A., Pajunen, H., Mäkelä, S. & Arvola, L. 2011: Carbon pools and fluxes in a chain of five boreal lakes: A dry and wet year comparison. J. Geophys. Res., 116, G03009, doi:10.1029/2010JG001636.

III) Einola, E., Järvinen, M. & Arvola, L. High summer discharge can carry more than half of the annual nitrate load from boreal catchments in southern Finland.
Submitted manuscript.

IV) Bärlund, I., Rankinen, K., Järvinen, M., Huitu, E., Veijalainen, N. and Arvola, L. 2009: Three approaches to estimate inorganic nitrogen loading under varying climatic conditions from a headwater catchment in Finland. Hydrology Research 40(2-3): 167-176.

V) Arvola, L., Hakala, I., Tulonen, T., Einola, E., Järvinen, M., Kankaala, P., Mäkelä, S.
TOC, N and P retention in a deep boreal lake (Pääjärvi, Finland). Manuscript.

THE AUTHOR'S CONTRIBUTION

I. The group jointly planned the study and interpreted the results. L. Arvola was responsible for writing the first version of the manuscript which was then commented by other writers.

II. The group jointly planned the study. E. Einola and S. Mäkelä did the fieldwork. E. Einola processed the data and wrote the manuscript which was then commented and processed further by the other writers. Einola finalized the paper.

III. The group jointly planned the study. E. Einola did the fieldwork. Einola processed the data and wrote the manuscript which was then commented on by the other writers. Einola finalized the paper.

IV. The group jointly planned the study. E. Einola partly collected the water quality data that was used in the study. Einola calculated the loads using methods developed in the Finnish Environment Institute and commented the manuscript.

V. The group jointly planned the study. E. Einola did part of the field work and collected water quality data. Einola did the first calculations of retention and took part in the writing process.

ABBREVIATIONS AND CONCEPTS USED IN THE THESIS AND THEIR DEFINITIONS:

C	Carbon
CO_2	Carbon dioxide
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
GWLF	General Watershed Loading Functions Model
INCA-N	Integrated Nutrients in Catchments – Nitrogen Model
NH_4	Ammonium
NO_3	Nitrate
P	Phosphorus
pCO_2	Partial pressure of CO_2
PO_4	Phosphate
TOC	Total organic carbon
TON	Total organic nitrogen
Tot N	Total Nitrogen
Tot P	Total Phosphorus

1. INTRODUCTION

1.1 A lake is a product of its catchment

For understanding biogeochemical processes of major nutrients (nitrogen, phosphorus and carbon) in lakes or in rivers, the surrounding catchment must be taken into careful consideration. A lake usually gathers most of its water from the catchment. Runoff waters transport various chemical compounds to the recipient water bodies, and catchment characteristics, land use and hydrological regime influence the magnitude and timing of their export. Already during transport the properties of chemical compounds are modified by biotic and abiotic factors. After entering the lake ecosystem biogeochemical processes continue. For instance, excess carbon dioxide as a product of community respiration (Striegl et al 2001) can be emitted to the atmosphere, while some proportion of particulate matter may settle in sediments and dissolved and suspended matter may continue their journey towards next lake.

1.1.1 Physiographical factors and runoff regime

According to Mustonen (1986) the runoff regime of a catchment is determined by six physiographic factors:

1) The basic characteristic of the catchment. For instance in small catchments the runoff peaks are steep, and if the shape of the catchment is round, the water accumulates rapidly. High lake percentage in the catchment smoothes both the high and the low flows.
2) Topography. In steep catchments water accumulates rapidly. In high altitudes precipitation increases while air temperature and evapotranspiration decrease.
3) The soil type and the bedrock. A large supply of ground water in the catchment acts as a lake by buffering against changes in the runoff.
4) Vegetation. The surface flow is slowed down in vegetated areas, and water is percolated rapidly into the soil with active root zone.
5) Land cover. E.g. forests buffer against changes in runoff and accordingly peat bogs reduce the runoff peaks but may also reduce the low flows because evapotranspiration is high.
6) Characteristics of the channel system. If there is an abundance of stream channels in the catchment the water accumulates rapidly. The slope of the channels also affects the water accumulation rate.

These physiographical factors form the framework in which the biogeochemical factors operate in the catchment. Climate is a driving force. The runoff regime is affected both by precipitation and temperature changes, as well as by changes in radiation balance (Korhonen & Kuusisto 2010).

In winter, precipitation is stored as snow in the boreal region and runoff is typically at its lowest. After that, the highest water levels and runoffs are typically recorded in springtime due to snowmelt (Mustonen 1986), and the highest nitrogen concentrations in rivers usually coincide with the increasing spring flows (Arheimer et al. 1996). Water levels and runoff usually decrease during summer when evapotranspiration is normally greater than precipitation, and in the dry and warm summers water levels can even be lower than winter minimums (Korhonen & Kuusisto 2010). In autumn, evapotranspiration is lower and precipitation increases water levels and runoffs.

1.1.2 The nutrients studied (N, P and Organic C) in the catchments, streams and lakes

1.1.2.1 Nitrogen (N)

Most boreal forests are nitrogen-limited and therefore efficiently retain nitrogen (N) (Lepistö et al. 2006). The reactions of N in the soil are complex and depend on prevailing conditions, e.g. moisture and oxygen conditions, temperature and pH. The most important reactions affecting the leaching are degradation of organic matter, nitrification, denitrification, ammonification, cation exchange and biological N fixation (Schlesinger 1997). The key factors controlling those reactions, and the export of N from the catchment, are hydrometeorological conditions, atmospheric N deposition, microbial activity, N uptake by vegetation and land-use practices (Wright et al. 2001, Goodale et al. 2002, Lepistö et al. 2008).

Organic N is biologically an important fraction of total N and it constitutes a major proportion of total N in forested boreal streams (Lepistö et al. 1995, Kortelainen et al. 1997, 2006, Mattsson et al. 2003). It´s proportion can also be significant in boreal rivers with mixed land use (Mattsson et al 2005) and in agricultural catchments (Heathwaite & Johnes 1996). Still, the inorganic fractions of N (nitrate, NO_3 and ammonium, NH_4) are considered to be the main N species influencing lake eutrophication (Wetzel 2001).

In many northern lakes, decreasing trend in the concentrations of inorganic nitrogen has been observed and the phenomenon has been connected to the decreasing N deposition (Rekolainen et al. 2005, Weyhenmeyer et al. 2007). However, in some of the long-term studies in boreal forest catchments no trends in inorganic and organic N concentration and transport in stream waters have been found (e.g. Sarkkola et al. 2012). In a study of eight lowland lakes having agricultural land on their catchments and situated in temperate and boreal regions George et al. (2010) reported increasing winter concentrations of NO_3 in all of the lakes.

1.1.2.2 Phosphorus (P)

Phosphorus (P) availability is regarded as the most important determinant of productivity and water quality in lakes (Dillon & Rigler 1974, Schindler et al. 1971, Schindler 1977)

The transport of P in soil depends strongly on the chemical properties of the soil. P can remain in the soil for long periods when bound in compounds with hydrated oxides of aluminium and iron. There are usually plenty of those oxides in clayey soils while in the peaty soils the binding of P is weaker (Hartikainen 1979). Organic matter reduces the binding of P because organic anions compete with P for the same oxide surfaces (Hartikainen 1979). In mineral soils the increase in acidity promotes the binding of P.

The P export from the catchments is usually in connection with soil erosion, but some P is always exported in its dissolved form in surface runoff and during floods (Schlesinger 1997). These events dilute the solution surrounding soil particles which leads to the release of P from the particle in order to maintain the same P concentration in the solution.

1.1.2.3 Organic carbon (Org. C)

Vegetation, climate and hydrological conditions are important factors contributing to the leaching of organic carbon (Org. C) from terrestrial ecosystems (Kortelainen 1999). Rivers and lakes transport, mineralize and accumulate significant amounts of terrestrially fixed allochthonous C (e.g. del Giorgio & Peters 1994, Kortelainen et al. 2004, Downing 2010).

In the boreal regions, the concentration of total organic carbon (TOC) in lakes and the export of TOC from catchments are strongly related to the coverage of peatlands (Kortelainen 1993, Kortelainen et al. 2006) and coniferous forests in the catchment area (Mattsson et al. 2003, Humborg et al. 2004). In Finnish forest streams and large rivers with mixed land use, more than 90% of TOC is in dissolved form (Mattsson et al. 2005, Kortelainen et al. 2006)

During the last decades, increasing concentrations of TOC and dissolved organic C (DOC) have been reported in many northern lakes and rivers (e.g. Vuorenmaa et al. 2006, Monteith et al. 2007, Sarkkola et al. 2009), but no evidence has been found for the increase in TOC export from the Finnish catchments (Sarkkola et al. 2009, Räike et al. 2012). The observed changes in TOC or DOC have been related to recovery from acidification and climate induced changes in DOC transport (e.g. Monteith et al. 2007).

1.2 Predicting future fluxes

In Finland, the current hydrological regime is characterised by temperature-sensitive snow-dominated seasonality. Even relatively modest increases in temperature can result in substantial changes in seasonal runoff patterns in snow-dominated areas (Arnell 1999, Barnett et al. 2005).

The annual mean air temperature in Finland has increased by about 0.7 º C since 1900 (Jylhä et al. 2004). In particular, spring months have become warmer (Tuomenvirta 2004). So far, statistically significant overall changes have not been found in mean annual discharge, but late-winter and early-spring mean discharges have increased in Finland during the period 1912 – 2004 (Korhonen & Kuusisto 2010).

According to different climate scenarios from several global models the average annual temperature in Finland is expected to increase by 2.0 – 6.5 °C by the 2080s and average precipitation by 7 – 26% (Jylhä et al. 2009). The model estimations predict that the most remarkable changes will occur in winter as the projected increases in winter temperatures are 3 -9 °C and precipitation 10 – 4 % and for summers 1 -5 °C and 0 -20%, respectively (Jylhä et al. 2009).

For differing climate scenarios the projected temperature increases are more consistent and more certain than predicted changes in precipitation (Barnett et al. 2005). Also in Finland, the clearest trends and changes in simulated future discharges have been related to an increase in air temperature rather than changes in precipitation (Veijalainen et al. 2010, Veijalainen et al. 2012).

Modelling results suggest that future fluxes of N, P and TOC are likely to change due to climate change in the boreal region. In the Pääjärvi catchment, even if significant changes are not projected for the annual fluxes of dissolved inorganic nitrogen (DIN), the projected warmer winters with increased precipitation will most likely result in higher streamflows and thus increased fluxes of DIN during winter time (Moore et al. 2010). For phosphate phosphorus, the simulated future changes in Pääjärvi catchment were also almost entirely associated with changes in winter precipitation (Pierson et al. 2010). Annual fluxes of DOC in Pääjärvi catchment were predicted to increase, partly due to increased decomposition but also due to higher winter streamflows (Naden et al. 2010, Jennings et al. 2010).

2. OBJECTIVES OF THE STUDY

This work is focused on the key nutrients, nitrogen, phosphorus and carbon, and how external factors influence their fluxes in streams and rivers and thus also control the annual and inter-annual dynamics in chemistry and biology of the recipient lakes. Four themes, each posing a question, are present throughout the study:

1) The seasonal (I, IV) and annual (II, IV, V) influence of climatic factors and hydrology on nutrient transport: i.e. how the seasonal and annual fluxes and concentrations of nutrients vary between years with differing precipitation, mean air temperature and discharge.

2) The impacts of "extreme event"-type of situations on nutrient concentrations: how nutrient concentrations of rivers react to changes in hydrology: wet vs. dry years (III).

3) The retention of nutrients in a boreal lake (V) and the influence of the catchment setting and size of the lake: how the upstream lakes affect nitrate concentrations and fluxes in streams (III), and what is the influence of the lake size on the fluxes of organic carbon (II).

4) The effects of climate change and land use on nutrient fluxes: to consider how climate change, land use and changes in it affect the nutrient fluxes in rivers and how it can be estimated (III and IV).

3. MATERIAL AND METHODS

3.1 Study sites

All the studied catchments are located within 50 km of each other, in the boreal region in southern Finland in the uppermost part of the Kokemäenjoki water course which drains into the Gulf of Bothnia, which is the northernmost arm of the Baltic Sea. The area lies between 180 m and 103 m a.s.l. The larger river catchments of Mustajoki and Haarajoki (I, III -V), and the small catchments of Löyttynoja and Koiran-suolenoja (III) drain into Lake Pääjärvi (V). The five lakes (II) Valkea-Kotinen, Alinen Rautjärvi, Ekojärvi, Kuohijärvi and Kukkia together form a lake chain and all are situated north of Lake Pääjärvi (Fig. 1).

The Pre-Cambrian bedrock of the area represents the deeply eroded root of the Sveco-Karelian fold formation (Laitakari 1980). There is an extensive veined gneiss zone with areas of granodiorite around lakes Pääjärvi and Alinen Rautjärvi, close to Lake Kuohijärvi and in the uppermost parts of the catchment of Mustajoki and Haarajoki (Laitakari 1964). The catchments of Löyttynoja and Koiransuolenoja have basic metavulcanic bedrock comprising amphibolite and tuffite (Laitakari 1964).

The surficial deposits of Mustajoki and Haarajoki catchments and the catchments of the lake chain are dominated by moraines. There is gravel and sand around Lake Alinen Rautjärvi and the river draining it, while clay areas partly surround lakes Kuohijärvi and Kukkia. The catchment area of the River Löyttynoja is characterized by highly permeable sand, gravel deposits, and peatlands. For the Koiransuolenoja catchment, fine sand, silt and moraine are the dominating soil types (Tikkanen et al. 1985).

The agriculture practised in the catchments areas is concentrated close to the river channels and consists typically of wheat, oat and barley crops and pasturelands. Potatoes and also sugar beet have been cultivated in the fields situated within the catchments of Löyttynoja and Koiransuolenoja. There is no point-source pollution in the study area but more than 90% of the peatlands are used for forestry and have been drained since the 1950´s with more recent small-scale ditch maintenance operations. Forests are typical coniferous Taiga forests dominated by Norway spruce (*Picea abies* [L.] H. Karst.) and Scots pine (*Pinus sylvestris* L.) with some deciduous species such as birch (*Betula* spp.), aspen (*Populus tremula* L.) and alder (*Alnus incana* L.).

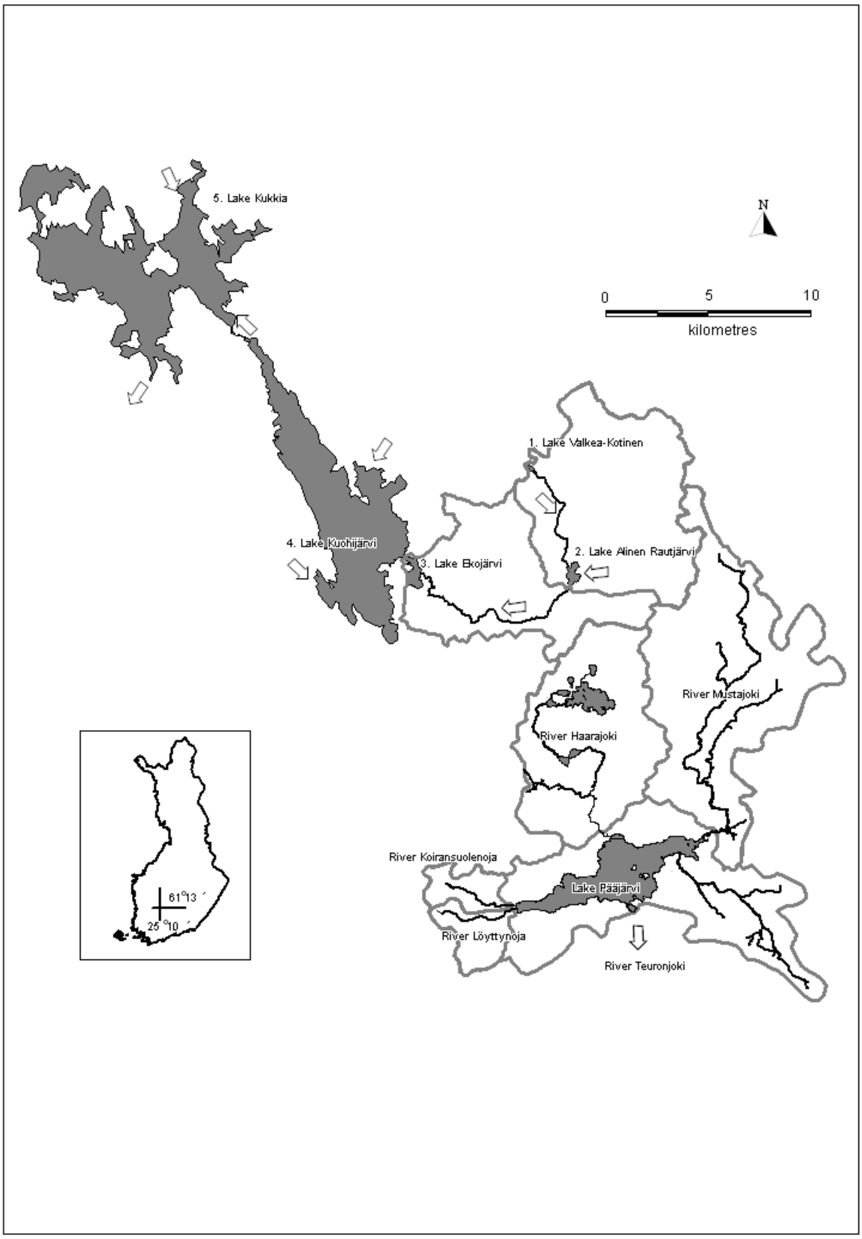

Fig. 1. The lake chain is situated north of Lake Pääjärvi and its rivers, with the catchments bordering each other. Lakes are coloured grey, rivers are black and the catchment boundaries are grey. The arrows indicate the direction of the water flow and in the lake chain, also the inlets of main rivers running to the study lakes are shown with the arrows.

The Koiransuolenoja catchment has the largest proportion of agricultural land whereas the highest peatland percentages are in the catchments of Mustajoki and Valkea-Kotinen (Table 1).

The highest mean concentrations of tot N are found in the River Koiransuolenoja while in the neighbouring River Löyttynoja the mean concentrations of tot N, and also tot P are lowest of the studied rivers (Table 2). There are no lakes inside the river catchments, except in Haarajoki. The Löyttynoja catchment contains a large ridge of glaciofluvial formations which accumulates considerable amounts of ground water (Tikkanen et al. 1985, Hakala et al. 2002). This store of water has a significant effect on the hydrology of Löyttynoja (Hakala et al. 2002). The geomorphology, topography and vegetation for catchments of Koiransuolenoja and Löyttynoja are described in more detail in Tikkanen et al. (1985).

Lake Pääjärvi is an oligo-mesotrophic lake, The lake has a maximum and mean depth of 85 and 15 m respectively and a surface area of 13.4 km^2. Its water has a brownish colour due to humic substances (Ruuhijärvi 1974, Arvola et al. 1996) and thus its photic zone is shallow.

Table 1. Properties of the land cover in the catchments studied in this work.

		Area (km^2)	Lakes (%)	Field (%)	Peatlands (%)	Forests (%)
(I, III, IV, V)	River Mustajoki	84	<1	13	20	67
(I, III, V)	River Haarajoki	58	6	11	12	71
(III)	River Löyttynoja	8	<1	17	14	69
(III)	River Koiransuolenoja	6.8	<1	24	5	71
(V)	Lake Pääjärvi	223	8	15	13	64
(II)	Lake Valkea-Kotinen	0.3	14	0	20	66
(II)	Lake Alinen Rautjärvi	8	6	0	16	78
(II)	Lake Ekojärvi	28	5	16	11	68
(II)	Lake Kuohijärvi	132	29	3	3	65

The lakes in the chain vary in their morphometry, and ratio of the lake area to catchment is clearly higher in the two largest lowland lakes than in the first three lakes in the chain (Table 1 in II). The concentrations of TOC, tot P, tot N and chlorophyll *a* are higher in the small upstream lakes than in the largest lowland lakes (Table 2). In the uppermost lake, Valkea-Kotinen, the hypolimnion is anoxic during winter and summer stratification. In Alinen Rautjärvi and Ekojärvi the hypolimnetic anoxia during the stratification periods is occasional, whereas in Kuohijärvi and Kukkia the entire water column remains oxic throughout the year.

Table 2. Chemical characteristics of water in the studied rivers and lakes. Mean ± standard deviation, in lakes at 1 m depth. The data for rivers and Lake Pääjärvi is from 2000-2007,analysed by Lammi Biological Station, and the data for the lake chain is from 1990 – 2009, Finnish Environment Institute (OIVA service on environment and geographic information, 17th March 2010, www.ymparisto.fi).

	tot N $\mu g\ L^{-1}$	tot P $\mu g\ L^{-1}$	TOC $mg\ C\ L^{-1}$	Fe $mg\ L^{-1}$	pH	Alkalinity $mmol\ L^{-1}$	Chl-*a* $\mu g\ L^{-1}$
River Mustajoki	1495 ± 757	37 ± 20	17 ± 7	1.5 ± 0.85			
R. Haarajoki	1359 ±923	42 ± 30	17 ± 6	1.1 ± 0.85			
R. Löyttynoja	1131 ± 339	26 ± 18	8 ± 6	1.5 ± 0.98			
R. Koirans. oja	2510 ± 1133	33 ± 29	9 ± 4	1.1 ± 0.65			
Lake Pääjärvi	1290 ± 175	11.8 ± 3.0	10.7 ± 1	0.15 ± 0.03	7.2 ± 0.2	0.27 ± 0.02	6.3 ± 3
L. Valkea-Kotinen	499 ± 88	17.7 ± 5.8	12.0 ± 2	0.27 ± 0.08	5.4 ± 0.2	0.013 ± 0.01	15.1 ± 10.7
L. A. Rautjärvi	482 ± 75	20.9 ± 6.4	10.4 ± 2	0.65 ± 0.19	6.5 ± 0.3	0.12 ± 0.03	16.4 ± 15.0
L. Ekojärvi	637 ± 146	18.3 ± 4.4	14.0 ± 2	1.1 ± 0.1	6.7 ± 0.3	0.15 ± 0.03	17.1 ± 14.4
L. Kuohijärvi	402 ± 42	7.2 ± 1.7	5.5 ± 0.4	0.06 ± 0.02	7.1 ± 0.1	0.18 ± 0.01	3.1 ± 0.5
L. Kukkia	339 ± 49	9.6 ±2.4	5.1 ± 0.3	0.05 ± 0.02	7.1 ± 0.2	0.20 ± 0.02	3.8 ± 1.2

3.2 Measurements and methods

Daily meteorological data have been collated since 1964 using a weather station established by the Finnish Meteorological Institute. The meteorological station is situated in the study area close to Lake Pääjärvi at the Lammi Biological Station.

3.2.1 Methods used for the studies done in Lake Pääjärvi and it's subcatchments (I, III - V)

Discharge has been recorded continuously using a measuring weir on River Mustajoki since 1971, River Haarajoki since 1972 and River Löyttynoja since 1970, and reported as daily mean values by the Finnish Environment Institute (SYKE). Daily runoff records for Löyttynoja cover 96%, for Mustajoki 93% and for Haarajoki 94% of the monitoring period 1978-2007 (III). Daily runoff data is available for the River Koiransuolenoja from 1967-1986. We estimated annual runoff for the 30-year period for all four rivers: linear regression between the discharge of the rivers Mustajoki and Haarajoki (R^2= 0.88, P<0.001) was used to derive the missing values for Mustajoki (years 1979-1980) and Haarajoki (October 2003 - November 2004) (III). Accordingly, linear regression between runoff in the River Mustajoki and the River Löyttynoja (R^2= 0.74, P<0.001) was used to derive missing runoffs for Löyttynoja (data missing for the year 1995). For Koiransuolenoja, linear regression with Löyttynoja was used (R^2= 0.78, P<0.001, missing years 1987-2007).

Samples for chemical analyses were collected weekly at river outlets (100-200 m upstream from the points where the rivers enter the lake) during the ice-free period and monthly or biweekly during winter in 1993-1999, and since the year 2000 weekly throughout the year. Samples were collected manually from the middle part of each river, using a 2 L-bucket with a long handle and pooling six to eight separate sub-sample lifts. In addition, samples were taken once a month from depth of 1 m at the deepest point of the lake (maximum depth 85 m), which is close to the outflow, and these values were used in budget calculations for the outflow (V).

Samples for NO_3, NH_4, tot N, phosphate (PO_4), tot P) and TOC were analyzed at the laboratory of the Lammi Biological Station using standard methods (e.g. APHA 1985).

River discharge and nutrient concentrations were used to determine the annual and summer loads. The weekly concentration data were linearly interpolated into daily values which were then multiplied by the daily discharge (most comparable to the method 2 in Rekolainen et al. 1991, see below), I, III - V).

Rekolainen et al. (1991) presented four different statistical standard methods to calculate load estimate: In the first method the concentration at the sampling time is multiplied by the discharge for the period after the sampling whereas in the second method the discharge period is chosen around the sampling time. According to the third method the annual load is the product of annual discharge and the arithmetic mean of the sampled concentration values and, in the fourth method the sampled concentration values are weighted with the flow at sampling times. Of these methods, Kauppila and Koskiaho (2003) found N loads estimated by the periodic method, i.e. method 2, to be most reliable but in general the results were quite similar for the different estimation methods. All four methods were included in the comparative study where estimates of NO_3 loads in Mustajoki by two different models GWLF and INCA-N were compared with each other and the statistical standard methods described above (IV).

GWLF (The Generalized Watershed Loading Functions) model (Haith & Tubbs 1981, Haith and Shoemaker 1987, Schneiderman et al. 2002) can be classified as a conceptual lumped parameter model (Leavesley 1999). It is a non-point source loading model which can be used to simulate monthly nutrient loads in stream flow. The model is driven by daily temperature and precipitation data. Daily water balance is simulated and water is partitioned among the different pathways of the hydrological cycle. The catchment is viewed as a system of different land areas (Hydrologic Response Units) that produce direct runoff, and two lumped (i.e. averaged over the whole catchment) subsurface reservoirs: an unsaturated soil zone from which water can be lost by evapotranspiration and a deeper saturated zone that maintains the base flow. Dissolved nutrient loads are derived by multiplying surface runoff and base flow by land-use specific nutrient concentrations.

The GWLF hydrology model was calibrated using precipitation and air temperature data from Lammi Biological Station for the time period 1982-2004 (Schneiderman et al. 2010, Pierson et al. 2010). Land use specific runoff concentrations were based on the long-term and intensively measured nutrient concentrations from the streams of small sub-catchments of the Lake Pääjärvi catchment area with distinct land use (see Hakala et al. 2002, Arvola, L. unpublished data). The time period 1994-2004 was used for nutrient calibration. Flow-weighted average nutrient concentrations were calculated and they were adjusted with the calibration factor of 1.01. This factor was obtained by minimizing the squared deviations between measured and simulated values in the time-series of flow-weighted concentrations (Pierson et al. 2010, Moore et al. 2010).

INCA-N (Integrated Nutrients in Catchments–Nitrogen) is a dynamic semi-distributed model that integrates hydrology and N processes (Whitehead et al. 1998, Wade et al. 2002, Wade 2004). The term semi-distributed refers to the description of catchment land surface which is not represented in detail, but rather by land-use classes in sub-basins. Sources of N include atmospheric deposition, leaching from the terrestrial environment and direct discharges. Terrestrial N fluxes are calculated in up to six user-defined land use classes. Hydrologically effective rainfall is used to drive the N through the catchment system and N can enter the river system by lateral flow through the surface soil layers or by vertical movement and transport through the groundwater zone (Rankinen 2006). Hydrologically effective rainfall is defined as that part of total incident precipitation that reaches stream channels as runoff and it is given as a daily input time series, which can be calculated by a hydrological model. Hydrology within the sub-catchments is modelled using a simple two-box approach, with reservoirs of water in a reactive soil zone and in a deeper groundwater zone. The mass balance equations for NO_3 and NH_4 in the soil and groundwater zones are solved simultaneously with the flow equations (Rankinen 2006). Key N processes that are solved in the soil water zone are nitrification, denitrification, mineralization, immobilisation, N fixation and plant uptake of inorganic N in the six land use classes. No biochemical reactions are assumed to occur in the groundwater zone. In the river the key N processes are nitrification and denitrification.

Hydrological input data (including hydrologically effective rainfall) was calculated with the watershed model WSFS (Watershed Simulating and Forecasting System) (Vehviläinen, 1994). The principles of the WSFS are based on the HBV model (Bergström 1976).The system uses meteorological and hydrological databases. In operational use the system provides flood forecasts on large river basins but in this study (IV) a more detailed calibration against observed discharge in the River Mustajoki was used.

INCA-N was calibrated with the River Mustajoki data. The model parameters of N fluxes in terrestrial and aquatic environments were adjusted to get simulated discharge and inorganic N concentrations close to observed data in the period 1995-2004. Simulated annual inorganic N fluxes in different land use classes were compared to plot scale values reported in literature or small research catchment studies. The model was calibrated with data from the period 1995-2002, and validated against data from the dry year 2003 and the rainy year 2004.The Nash-Sutcliffe efficiency for simulated discharge was 0.751 in the calibration period and 0.658 and 0.819 in the validation years. Values of the regression coefficient R^2 for the NO_3 concentration were 0.287, 0212 and 0.431, respectively (IV).

3.2.2 Methods used in the study of the lake chain (II)

Carbon fluxes, including inputs from the catchment, atmospheric deposition, and output of TOC and dissolved inorganic C (DIC), efflux of CO_2 to the atmosphere, as well as net sedimentation of C and net primary production (NPP) of phytoplankton and littoral macrophytes, were calculated for the four uppermost lakes in the chain (Valkea-Kotinen, Alinen Rautjärvi, Ekojärvi and Kuohijärvi) to establish a carbon budget for each lake. For the fifth lake in the chain (Kukkia) the dataset was not sufficient for budget calculations, because the carbon inputs from the catchment were not determined. The calculations were carried out for the years 1997-1998.

The samples for TOC and DIC analyses of the water column were taken at a depth of 0.2-0.5 m in rivers connecting the lake chain and at 1 m depth in the lakes. The sampling frequency in the rivers was primarily once a month during the open water season (May – November) and once in winter (early April). The uppermost lake (Valkea-Kotinen) was sampled 24 times during both years. The other lakes in the chain were sampled 1-4 times in 1997 and four times in 1998 (late winter, spring, summer, and autumnal mixing). For the missing data for spring 1997 in Alinen Rautjärvi and Kukkia, and for winter, spring and autumn 1997 in Kuohijärvi the values for the corresponding season of 1998 were used.

The discharge from each subcatchment was estimated using measured daily runoff data from the rivers Mustajoki and Haarajoki, assuming that the discharge from each subcatchment was related to its area. The TOC and DIC input and output were calculated by multiplying the monthly discharge (the sum of measured daily values) at the inflows and outflows with the TOC and DIC concentration during the respective period in the rivers between the lakes. The min – max range of the annual TOC and DIC loads to lakes were estimated by multiplying monthly discharge with minimum concentration (annual mean – SD) as well as maximum concentration (annual mean + SD) of TOC and DIC of both years. For the uppermost lake in the chain, the input of TOC and DIC from the catchment was estimated using the values of small brooks having the similar catchments with no upstream lakes.

Emissions of CO_2 from the lakes were calculated using the equation by Cole & Caraco (1998), in which the CO_2 saturation in the surface water was compared to the equilibrium value. The CO_2 concentrations were calculated from the available open-water DIC and pH results of each lake, with correction for water temperature (Stumm & Morgan 1970, Butler 1982, Kling et al. 1992). Partial pressure of CO_2 (pCO_2) was calculated from the CO_2 concentrations, using Henry´s law constants corrected for temperature and atmospheric pressure (Plummer & Busenberg 1982). The equilibrium CO_2 concentration in the lake water was calculated using Henry´s law constants, assuming an atmospheric mixing ratio of 361 parts per million by volume (ppmv) for 1996 and an annual increase of 1.5 ppmv a^{-1} (IPCC 2001) and the elevation of the lake. The piston velocity of CO_2 was obtained by first determining the piston velocity of SF_6, using the empirical relationship between the piston velocity of SF_6 normalized to a Schmidt number of 600 and the windspeed at a height of 10 m (Cole & Caraco 1998) and then calculating the Schmidt number for CO_2, using empirical third-order polynomial fits to temperature (Jähne et al. 1987). The windspeed was assumed to be 3 m s^{-1}, which is the average long-term open-water period windspeed for inland measurement stations in Finland (Leinonen 2000). All the equations for calculation of the CO_2 emissions are presented in Rantakari & Kortelainen (2005). The estimates of CH_4 emissions from some of the study lakes were minor compared to CO_2 efflux (Kankaala et al. 2005, 2006; Bergström et al. 2007). The measured atmospheric deposition of C in the area was 1 g C m^{-2} a^{-1} (Kortelainen et al. 2006).

The primary production of phytoplankton in Lake Valkea-Kotinen was measured weekly during the open-water season *in situ* using the ^{14}C method (Keskitalo & Salonen 1994). Since the incubation time was 24 h, the measurements resulted in net primary productivity values (NPP). For the other lakes, the range of NPP of phytoplankton was estimated using data obtained in previous measurements in neighbouring lakes (Ilmavirta & Kotimaa 1974, Arvola 1983, 1984, Arvola et al. 1999), with the same types of trophic status and chemical and physical properties as in the study lakes. The areas covered by different macrophyte species were mapped in 1997 – 2000 (Huitu & Mäkelä, and Mäkelä, unpubl.). The macrophyte C pool was estimated as a seasonal maximum biomass (g dry weight m^{-2}) converted to C by a factor 0.38 (Duarte 1992), obtained from the data for stands of the dominant species in the three uppermost lakes (Keskitalo & Heitto 1996, Kankaala et al. 2003, 2005). The NPP of macrophytes was estimated to be twofold the seasonal maximum biomass of all the stands (Westlake 1982).

We also made a regional, landscape-scale estimate of CO_2 emissions and sediment C net accumulation of all the lakes in the cumulative catchment area of the lake chain. The results from the five lakes were generalized for the respective lake size classes (area < 0.1, 0.1 – 1, 1 – 10 and 10 – 50 km^2) throughout the area. The areal results (g C m^{-2}) of the largest size class were also applied to the size class 1 – 10 km, because none of the studied lakes in the lake chain belonged to that size class.

4. RESULTS AND DISCUSSION

4.1 Annual and seasonal variation in nutrient concentrations and fluxes due to climatic factors and hydrology

The annual long-term (1987 – 2007) average precipitation in the area is 632 mm (SD=88 mm) (Finnish Meteorological Institute). For the 30 year period of 1978 - 2007, summer runoff, as well as precipitation were lowest in 1999 and highest in 2004. The summer precipitation of 1998 was ranked third highest for the 30- year period, while summer 1996 had high runoff albeit summer precipitation was close to the mean. Compared to the long-term mean, the mean daily air temperature was always lower in wet (or high discharge) summers and higher in dry (or low discharge) summers (Table 3).

Table 3. Annual, summer (June-August) and long-term (1978-2007) precipitation, mean daily air temperature and mean runoff in Mustajoki catchment. The "wet" years with either high precipitation (in II) or high runoff (in III) are shown as bold with gray shadowing and the "dry" years with low precipitation (II) or low runoff (III) are shown as bold with white background.

	Annual			Summer (June-August)		
	precipitation	temperature	runoff	precipitation	temperature	runoff
	mm	°C	L s^{-1} km^{-2}	mm	°C	L s^{-1} km^{-2}
1995	659	4.7	8.6	151	15.9	3.1
(III) 1996	**593**	**3.5**	**7.6**	**195**	**14.7**	**10.7**
(II) 1997	**598**	**4.3**	**6.1**	**200**	**16.5**	**5**
(II, III) 1998	**766**	**4.1**	**10.3**	**368**	**14.7**	**10.7**
(III)1999	**587**	**5.1**	**8.1**	**120**	**17.4**	**1.5**
2000	634	5.8	9.1	266	14.7	3.1
2001	496	2.9	6.9	153	14.8	6.1
(III)2002	**535**	**6.8**	**4.9**	**209**	**17**	**2.8**
(III 2003	**618**	**4.3**	**4.4**	**189**	**15.6**	**2**
(III) 2004	**798**	**4.4**	**10.2**	**413**	**14.4**	**16.2**
2005	572	5	6.5	234	15.5	4.3
long-term (1978-2007)	632	4.2	9.2	224	15.1	6.3

The highest runoff peaks are generally observed in spring after snowmelt or during autumn, when precipitation is generally higher than in summer and the evapotranspiration is small. However, high runoffs can also occur during summer, as in 1996, 1998 and especially in 2004 (Table 3), if the precipitation is high and the antecedent soil conditions are wet.

4.1.1 *N and P*

In Mustajoki and Haarajoki the highest concentrations of Tot N, NO_3, NH_4 and Tot P were often found in spring (April-May) and late autumn (November-December) and the lowest in summer (June-August) and autumn (September-October) (I). The runoff conditions did not affect nutrient concentrations in spring, while in summer, autumn and late autumn the impact was strong. In both rivers, discharge rates explained 60% - 70% of the variation in Tot P and Tot N concentrations in autumn and late autumn.

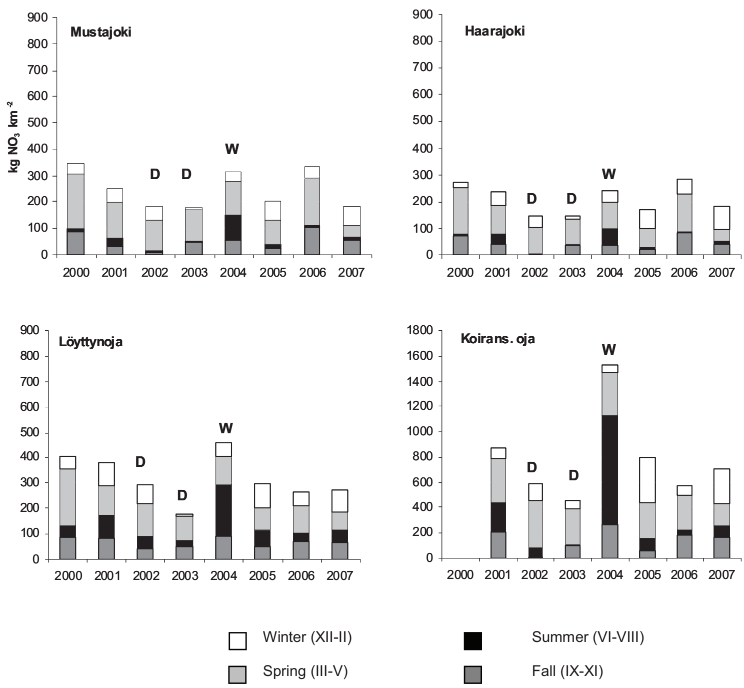

Fig 2. Calculated annual loads of NO_3 in the four rivers (III). Dry, low discharge summers are marked with D and wet, high discharge summers with W. Note the different scale for Koiransuolenoja.

The calculated seasonal and annual loads of NO_3 varied between the years and the rivers (Fig. 2). Although very small fractions of annual loads were comprised by summer loads especially in dry summers, the annual loads remained low during the years with dry summers. This also highlights the importance of antecedent soil moisture conditions: after a dry summer the autumn runoff was not usually high, either.

The model estimates of annual loadings of dissolved inorganic nitrogen (DIN) in Mustajoki varied from 120 to 570 kg km^{-2} a^{-1} during the study period of 2000-2004 (IV). With the INCA-N model the difference to the reference method (Rekolainen et al. 1991) was highest in the wet years 2000 and 2004 when summer and late autumn discharge was high. The GWLF model estimation for the DIN load was close to the level given by the reference method, except in the years 2001 and 2002, when the model was not able to reproduce the spring discharge maximum properly.

The retention of Tot P per unit area in Lake Pääjärvi was higher during high runoff and short lake residence time but no similar relationship was found between Tot N and residence time. However, time-lags in hydrology complicate the calculations when the lake residence time is much longer than one year (in Pääjärvi the theoretical residence time varied between 2.1 and 5.7 years).

4.1.2 C

Hydrology was an important driver of C transfer from the catchment and along the lake chain: the annual TOC loads from the catchments into the lakes increased by 40 – 210% in the wet year 1998 compared with the dry year 1997 (II). The increased runoff in 1998 was the main determinant for the higher loads, whereas the higher concentrations of TOC in river water in summer 1998 (average 14.7 mg C L^{-1}) compared with those in 1997 (average 10.8 mg C L^{-1}) had a minor role.

The annual input of C by the net production of macrophytes was always small compared with the C input to the lake by runoff (cf Fig. 4). The net production of macrophytes was lower than the estimated net primary production by phytoplankton in each lake. With the exception of the uppermost headwater lake Valkea-Kotinen during the dry year, C input from the catchment exceeded the autochthonously produced C in the lakes.

The C budgets of the lakes were negative in the dry year (1997), presumably indicating losses of C that had been formerly accumulated in the lakes. During the wet year, the three lakes along the chain acted as sinks of C, probably replacing the lake water C pool that had been decreasing during the preceding dry year. The output of C in the uppermost lake clearly dominated over the input, as was also noted in a small nearby lake by Arvola *et al.* (1990). This was possibly due to the difficulties in determining the amount of the C input from the catchment in the small lakes without inlets. Thus, our presumption of groundwater being an insignificant source of C may also have been wrong in Lake Valkea-Kotinen, since a strong groundwater signature in aquatic pCO_2 has been found in many lakes and streams in Sweden by Humborg *et al.* (2010).

During the rainy year 1998, the CO_2 emissions were higher than during the dry year in the three smallest upstream lakes. Rantakari & Kortelainen (2005) also found a close connection between annual CO_2 emission and precipitation in large Finnish lakes, and suggested that more organic carbon produced in the terrestrial ecosystem is transported to the lakes and decomposed during periods of high precipitation. Ojala et al. (2011) and Linnaluoma (2012) reported extremely high CO_2 emissions during or just after heavy rains in summer. In the study by Rantakari & Kortelainen (2005), also the importance of the weather conditions of the previous autumn was emphasized, as they contributed to the delay between heavy rainfall in the autumn and increasing CO_2 concentrations in the winter in large Finnish lakes. This may have influenced our largest study lakes, Kuohijärvi and Kukkia, which have long residence times and large water volume. In these two lakes, the CO_2 emissions were higher during the dry year.

In the lakes in the chain (Valkea-Kotinen, Alinen Rautjärvi, Ekojärvi, Kuohijärvi) the retention of C ((sedimentation + atmospheric emission) / C input) was more efficient in the dry year. This was presumably related to the longer hydraulic residence time during the dry year, providing longer time periods for sedimentation as well as for the biogeochemical and physical mineralization processes.

4.2 The impacts of "extreme event"-type situations

The concentrations of NO_3 in Haarajoki river and Koiransuolenoja river were significantly higher in wet (high discharge) summers than in dry (low discharge) ones, but in Löyttynoja river and Mustajoki river the mean concentrations were higher in dry summers than during wet ones (III). In Mustajoki, NO_3 concentrations remained low during the wet summer of 2004, e.g., if compared to the dry year 1999, except during the two periods of maximum runoff (Fig. 3). However, during the second runoff peak in late July, which was even higher in magnitude than the first one, NO_3 concentrations were clearly lower than during the first peak. The same was found for NO_3 in river Haarajoki in 2004.

The flux of NO_3 from the catchment was significantly higher in wet summers than in dry summers. In Mustajoki, Haarajoki and Koiransuolenoja the NO_3 fluxes during dry summers were on the average 5-13% of the wet summer fluxes. The difference between dry and wet summers was clearly lower in Löyttynoja where the NO_3 fluxes during the dry summers were, on average, 39% of the wet summer fluxes.

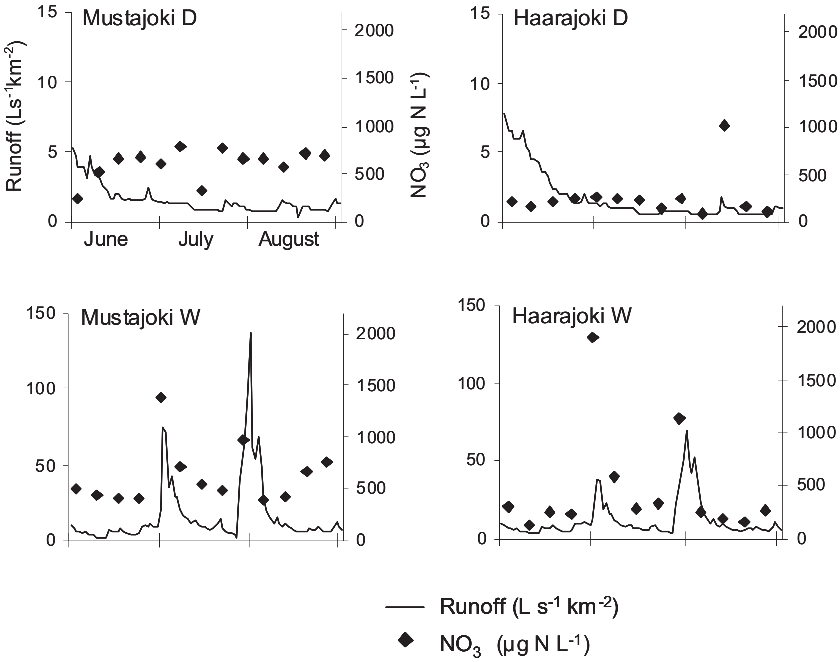

Fig. 3. Runoff and concentrations of NO_3 during the driest summer (D) 1999 and the wettest summer (W) 2004 in Rivers Mustajoki and Haarajoki (III). Note the difference in the runoff scales.

The contribution of the summer NO_3 fluxes to the annual NO_3 fluxes varied between the study years and rivers. In the dry summer of 2003 the flux comprised only 1% of the annual flux in Haarajoki, and in Mustajoki and Koiransuolenoja 4% and 2%, respectively. In Löyttynoja the summer contribution was always >10% of the annual flux. In the wet summer of 2004 the NO_3 flux comprised 57% of the annual flux in Koiransuolenoja, and 44%, 32% and 26 %in Löyttynoja, Mustajoki and Haarajoki, respectively. This demonstrated that stormy weather with high precipitation substantially enhanced NO_3 leaching at a time when surface and subsurface runoff predominate. Similarly, Bechtold et al. (2003) observed that hydrological factors largely controlled N fluxes in a floodplain of temperate forest, as nitrate was rapidly leached from soils during rainstorms. These results suggest that extreme weather conditions that are projected to be more common in future (e.g Beniston et al. 2007) can fuel inorganic nutrients to lake ecosystems during the growing season, which may lead to immediate response in primary production and/or community composition and competition of phytoplankton, in particular if the system is N-limited.

Our results indirectly suggested that the storages of nitrate might deplete in the course of the summer rainstorms in the studied catchments, because NO_3

concentrations did not increase despite further increases in runoff (Fig. 3). This would be reasonable because the accumulation of soil nitrate occurs over dry periods as has been shown by Bechtold et al. (2003), and therefore flushing may rapidly decrease the N pool in the upper soil layers.

4.3 Retention of nutrients in boreal lakes and the influence of catchment setting and lake size on nutrient fluxes

Upstream lakes have been shown to decrease the concentrations of particulate P (Arheimer & Lidén 2000), Tot N and Tot P (Rantakari et al. 2004) and TOC (e.g. Kortelainen 1993, Rantakari et al. 2004) in rivers and also to decrease riverine loads of NO_3 (Arheimer et al. 1996) and TOC (e.g. Mattsson et al. 2005).

For the River Haarajoki, the upstream lakes lowered the NO_3 concentrations during the dry summers and also reduced the proportion of NO_3 to total N. River Haarajoki was a clear exception among the studied rivers because the minimum NO_3 concentrations of the river were at least one order of magnitude lower than in the other rivers.

The mass balance calculations for Lake Pääjärvi showed that the mean annual retention for Tot P in the lake was as high as 74% while the values were lower for Tot N (27%) and TOC (34%). It is evident that Pääjärvi lowers the nutrient concentrations downstream. The mean retention of TOC in Lake Pääjärvi was 22 g C m^{-2} a^{-1}, which was very close to the value for Lake Kuohijärvi where TOC outflow subtracted from allochtonous TOC resulted in 18 g C m^{-2} a^{-1}, (see Table 6 in II), during the rainy year. Mattsson et al. (2005) calculated the mean TOC retention of 15 g C m^{-2} a^{-1} in their large dataset of Finnish river basins with upstream lakes covering on average 9% of catchment area.

Hydrological import and export of TOC dominated the carbon fluxes especially in the two small drainage lakes in the middle of the chain (Fig.4, II). Atmospheric emissions were highest in the three uppermost lakes during the wet year. The in-lake processes presumably had greater influence on the C fluxes in the large lakes of our study, while in the small drainage lakes the allochthonous matter dominated.

On the landscape scale, the small lakes (area < 1 km^2) were important in the net accumulation of carbon in the sediments, since they were responsible for 56% of the net C accumulation in all the lakes although they formed only 14% of the entire lake area. On the other hand, the large lowland lakes (size class 10 – 50 km^2) played a more important role in the CO_2 emissions. In the dry year, the emissions from these lakes made up 60% of the total C effluxes from all lakes in the area.

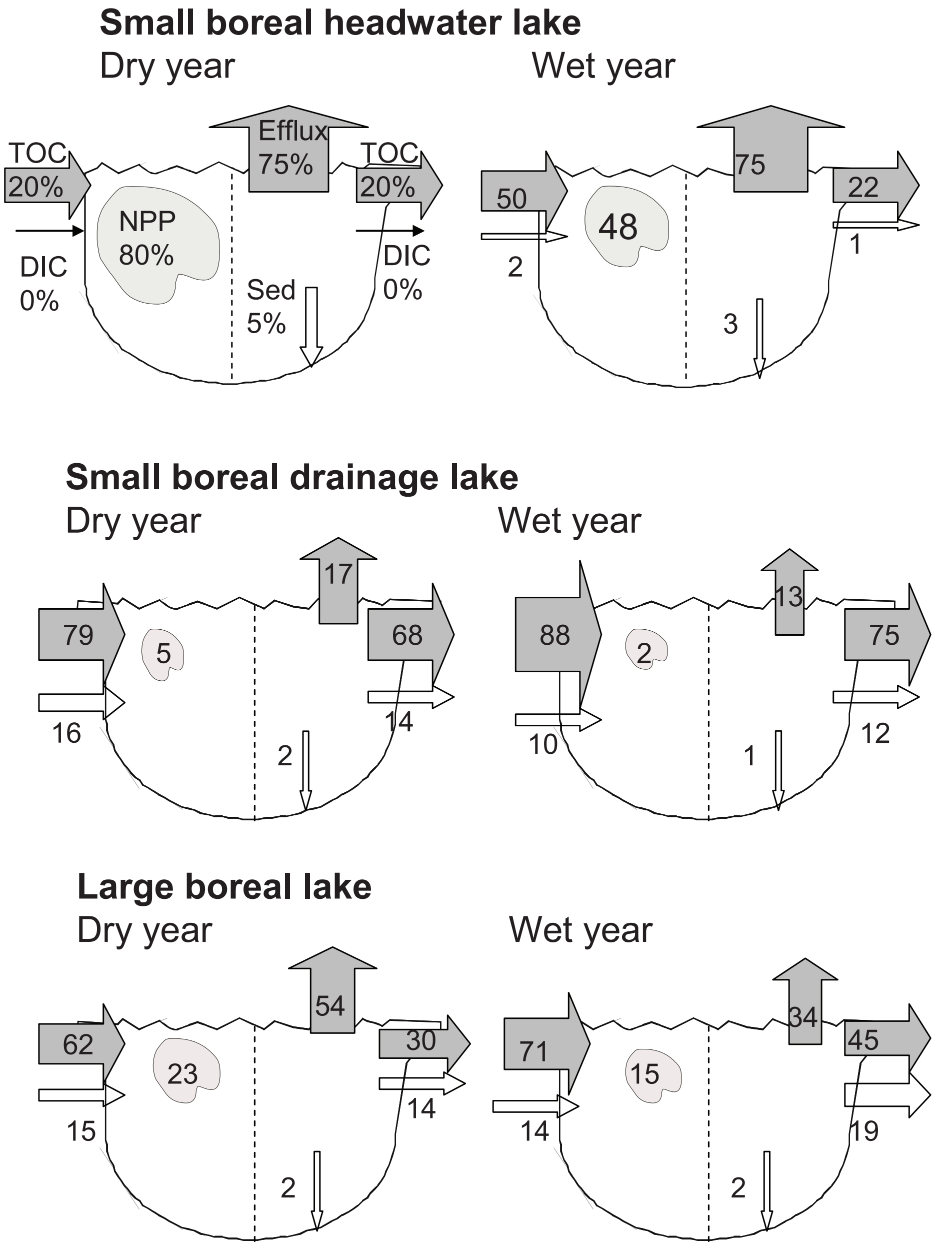

Fig. 4 A conceptual figure showing the influence of annual precipitation conditions on the proportionation of carbon fluxes in different types of lakes in our study (II, © John Wiley and Sons 2011). The inputs are shown on the left and the outputs on the right sides of each basin. The values are percentages of the total inputs and outputs. NPP is the net primary production of phytoplankton and macrophytes.

4.4 The effects of climate change and land use

In the four rivers the NO_3 concentrations were closely related to the proportion of land area used for agriculture (III), and therefore possible future increase in agricultural land area in Finland (Audsley et al. 2006) may enhance NO_3 fluxes to rivers and lakes, and finally to the Baltic Sea.

Peatland carbon sequestration rates are highly sensitive even to minor climatic fluctuations (Yu et al. 2003), with wet periods correlating rapidly with peat accumulation. Similarly, the soil organic carbon pool in Nordic forest soils increases with both mean annual temperature and mean annual precipitation (Callesen et al. 2003).

The increasing trend in stream water TOC concentrations has been connected to rising temperature in boreal forested rivers (Sarkkola et al. 2009, but see Erlandsson et al. 2008). In our study water temperatures of all the lakes in the chain were higher during the dry year, which may also have impacted on the higher CO_2 fluxes to the atmosphere (II). Kosten *et al.* (2010) found that the pCO_2 closely followed the temperature in 82 South American lakes having wide ranges in DOC concentrations, suggesting an increase in temperature-dependent mineralization of DOC and larger CO_2 emissions from lakes due to climate warming.

According to the regression model estimations (I) a doubling in discharge could result in a 10%, 13%, 23%, and 33% increase on an annual basis in the concentrations of NO_3, Tot N, PO_4 and Tot P, respectively. The highest increase would take place in autumn, when the concentration of Tot N could increase more than 50%.

The increasing frequency of heavy precipitation events and wet/dry periods may further strengthen the variability in timing and magnitude of loads of N (Moore 2010), P (Pierson 2010) and C (e.g. Hongve et al. 2004, Erlandsson et al. 2008). Naden *et al.* (2010) showed that the future model projection (for years 2071-2100) for the Mustajoki River includes a 7% increase in annual mean DOC concentrations and a 16% increase in annual mean DOC load.

Models are needed to forecast future nutrient loadings (Carpenter 2003, Pierson 2010). Under the current situation dominated by snow-melt, both INCA-N and GWLF seemed to give congruent annual loading estimates of dissolved inorganic nitrogen (IV). However, the loading estimates differed between the studied methods in years when snowmelt was not the dominating hydrological pattern (INCA-N in 2000 and 2004) or when the model was not able to reproduce the spring discharge maximum properly (GWLF in 2001 and 2002). It seems that to capture the loading that is based on weekly measurements, the model performance concerning hydrology is more important than the reproduction of the temporal concentration dynamics of dissolved inorganic nitrogen.

There will evidently be variation in the response of lakes and rivers to climatic drivers, as also shown in our analysis. This will largely depend on the characteristics of the lakes and rivers itself as well as on the properties of their catchments.

5. CONCLUSIONS

In rivers in the boreal region the air temperature and precipitation can explain a high proportion of the annual and seasonal variability in nutrient concentrations. However, the relationships between the weather and water quality are often masked by time lags in hydrology, seasonality and complexity of all the affecting factors.

The significant role of the discharge on NO_3 concentrations and loads was emphasized during summers of contrasting hydrology. The highest concentrations in river NO_3 were found during the high discharge summers, and contribution of the summer NO_3 load to the annual load was up to 57% in the summer of high discharge. This kind of increase in NO_3 load evidently causes remarkable changes on the nitrogen levels in a recipient lake, effecting it's ecosystem during the growing season.

More detailed observation on the variation in NO_3 concentrations in summers brought up the special characteristics of individual rivers, highlighting the effects of land use, land cover and ground water deposits on water NO_3 concentrations. It was also suggested that the storage of nitrogen in the boreal soils is seldom infinite and there is most probably a point where an increase in runoff will not cause an increase in the concentrations.

Models are needed to forecast future nutrient loadings. In order to capture the loading with the dynamic models INCA-N and GWLF, model performance concerning hydrology seems to be more important than the reproduction of the temporal concentration dynamics of dissolved inorganic nitrogen.

The annual retention of N in Lake Pääjärvi was highly variable, ranging between -0.5% and 51%. For P the retention was 64 -88% and for organic C 11-59%. These values provide evidence for the effects of the lakes in the catchment on decreasing the nutrient concentrations downstream.

The effects of the lake size and its setting on the catchment were highlighted in the study of C in a chain of lakes. Hydrological import and export of TOC dominated the carbon fluxes in the small drainage lakes while in-lake processes had greater influence on the C fluxes in the large lakes. On the landscape scale, small lakes were important in the net accumulation of carbon in the sediments, and the large lowland lakes played a more important role in the fluxes of CO_2 to the atmosphere.

The results of these studies indicate that inter-annual climatic variability may strongly affect ecosystem nutrient cycling, but there will be variation in the response of lakes and rivers, depending on the characteristics of the catchments and the lakes and rivers itself.

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